



Hydrotropes



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ABSTRACT

The concepts “hydrotrope” and “hydrotropy” are reviewed with a strong focus on the literature from recent years. The action and physical–chemical behavior of hydrotropes are discussed in relation to co-solubilizers and surfactants. A definition of a hydrotrope is formulated, and it is demonstrated that the unique behavior of a hydrotrope, which distinguishes this class of substances from both co-solubilizers and regular surfactants, is that the aggregation is weak without a hydrophobic solute, but there is a pronounced aggregation in the presence of a hydrophobic solute.

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1. Hydrotropes versus co-solvents, co-solubilizers, and surfactants

Exactly 100 years ago, the term “hydrotrope” was coined by Neuberg, for compounds that increase the solubility of sparingly soluble organic substances in water [1]. “Hydrotropy” has later been introduced to describe the action of a hydrotrope.

The definition seems simple but is in reality not unambiguous. There are many ways by which the aqueous solubility of a hydrophobic organic molecule can be raised: use of a water miscible solvent, addition of a salting-in electrolyte, use of an antagonistic salt, i.e., an electrolyte consisting of a large organic (lipophilic) ion and a small inorganic (hydrophilic) ion, addition of a surfactant that will solubilize the hydrophobic substance in the micelle core (or in the palisade layer, if the substance is of medium polarity), and addition of a combination of a surfactant and an oil in order to solubilize the substance in a microemulsion.

How can we find order in this multitude of solubilization phenomena? Following the ideas of Abbott, et al. [2,3,4^{••}], we suggest a classification based on the structuring of the ternary mixtures water–hydrotrope–hydrophobic substances: *A hydrotrope is a substance whose structuring in water is enforced by the presence of a third, water-immiscible compound (property A)*. As a corollary of this enforced structuring, the solubility of the hydrophobic compound is enhanced.

There is a strong similarity between an aqueous hydrotrope solution and a hydrotrope mixture with an organic solvent. Binary systems of an organic, water-immiscible solvent (e.g., octanol) and a co-solvent (e.g., ethanol) may or may not exhibit structuring. *A hydrotrope is then a substance, whose structuring in the organic solvent is enforced by the presence of water (property B)*. As a corollary of this enforced structuring, the solubility of water in the solvent is enhanced.

Considering this definition only, all surfactants or “detergents” would belong to this category. Indeed, the classical series of papers by

Winsor, 60 years ago, was entitled “Hydrotropy, solubilisation and related emulsification processes” [5[•]]. At that time, the distinction between hydrotropy and solubilization in micelles and microemulsions was not clear [6]. Since then, it is evident that emulsification is related to two-phase systems, whereas solubilization can be attributed to either surfactants or hydrotropes. The definition of a hydrotrope that we use in the present review is the following: *a hydrotrope is a substance that show property A and/or B and does not form a microemulsion or lyotropic liquid crystal*.

Microemulsions and liquid crystals are thermodynamically stable structures at meso-scale; in both cases, the total interfacial area per unit volume is fixed by the amount of surfactant.¹ In the case of hydrotropes, the presence of a well-defined interface between water-rich and oil-rich domains is not necessary, and not known a priori from the composition.

Nanostructures formed by microemulsions show intense scattering including a large q asymptotic limit, while in the case of hydrotropes, this q^{-4} power law of the scattering cannot be observed. Thus, although there is a structuring in hydrotropic systems, the nanostructures are much less defined, and the difference between microemulsions and systems based on hydrotropes can be clearly seen in SAXS or SANS

¹ Note that the use of regular surfactants is not covered in the review. This topic is treated in text books and book chapters, e.g. [9,10]. Neither is the use of a hydrophilic surfactant, such as a short chain alkyl glucoside or a phosphate ester, to improve the solubility of a hydrophobic nonionic surfactant discussed in the review. The surfactant used for this purpose is often referred to as a ‘co-surfactant’, but the term hydrotrope is also used. The effect exerted by the hydrophilic surfactant in such formulations is often measured as the ability to raise the cloud point of the formulation. The role of the co-surfactant may also be to reduce the liquid crystalline domain of the hydrophobic surfactant–water system. These are practically important effects and co-surfactants (hydrotropes) are frequently used in industrial cleaning formulations. The topic is extensively treated in other reviews [11,12].

scattering spectra. Note that the free energy differences between an organic molecule inside and outside the structures are also significantly different. They are of the order of 5–9 $k_B T$ (10–25 kJ/mole) in the case of a microemulsion, and only around 1 $k_B T$ or even less in the case of typical hydrotropes.

On the thermodynamic level, the distinction between surfactants and hydrotropes is given by the concentrations used. Whereas it is of the order of millimolar or less for surfactants (the critical micellar concentration, CMC), it is in the molar range for hydrotropes (the minimum hydrotrope concentration, MHC). Accordingly, the surface tension decrease of aqueous hydrotrope solutions requires these higher concentrations. Note, however, that the minimum surface tension in concentrated hydrotrope solutions can be as low as in conventional surfactant solutions. A value as low as 27 mN/m has been reported [7].

With the definition of a hydrotrope given above, we can also make a distinction between a hydrotrope and a co-solvent, both on the nano-scale and on the macroscopic, thermodynamic level: adding an organic substance to a mixture of water and co-solvent will not significantly alter the structuring of the solution. On the thermodynamic level, the consequence is that there is no minimum co-solvent concentration; instead, the solubilization of the organic substance will progressively increase (although not necessarily linearly) with increasing co-solvent concentration. Therefore, we call sodium xylenesulfonate (SXS) a hydrotrope, and acetone a co-solvent, according to the results given in [8•]. Structures of some typical hydrotropes are given in Fig. 1.

However, as always with classifications, there are cases that are borderline, and indeed, as regards hydrotropes, there are even many of them. This has two reasons: on the one hand, there is a continuous cross-over from co-solvents to hydrotropes (it is difficult to define unambiguously, in which case an MHC exists) and from hydrotropes to surfactants [13,14] and on the other hand, there are simply not enough structural data to conclude whether or not a ternary mixture is in agreement with the above definition.

And there is a further complication: depending of the relative concentrations in the ternary mixture, a component can either be a co-solvent or a hydrotrope. As discussed in detail in the paper by Schöttl and Horinek in this issue, highly fluctuating structures appear in the

ternary systems consisting of water–ethanol–*n*-octanol, whenever the composition is not too far away from the demixing boundary (the so-called *pre-Ouzo* region) [15•]. In this case, ethanol partitions between the two pseudo-phases (one rich in water, the other rich in octanol) with a slight accumulation of ethanol at the interface. Here, the ethanol behaves somewhat like a hydrotrope, and the free energy differences between ethanol in either the aqueous or the organic pseudo-phase and at the interface are, although important and significant for the structuring, only of the order of less than 1 $k_B T$. Note that this structuring and the energies related with it can be significantly enhanced by adding antagonistic salts, e.g., $(C_6H_5)_4PBr$ or $NaB(C_6H_5)_4$ [16•]. They have a strong propensity to go to the interface and rigidify it in the presence of co-solvent. To a minor extent, this occurs also with simple salting-in electrolytes such as NaSCN. Note that antagonistic salts alone can also act as solubilizers, as is discussed in the manuscript by Onuki in this issue. If an antagonistic salt is added to such a ternary system in the *pre-Ouzo* regime, the combination of co-solvent and salt can even behave as a true surfactant, giving X-ray and neutron scattering fingerprints similar to those of SDS micelles. We will come back to this point in Section 3.

We should recall here that both hydrotropes and surfactants can be charged or uncharged. In an analogous way, we can extend the definition of co-solvents: they can be neutral, as ethanol, or they can be charged. In the latter case, they are usually termed “salting-in” electrolytes. According to the seminal paper by Long and McDevitt [17], salts like CsI and $HClO_4$ and to a much larger extent $(CH_3)_4NCl$ significantly enhance the solubility of hydrophobic molecules in water. In a formal sense, they can consequently be included in a more general definition of co-solvents. Maybe “co-solubilizers” is an appropriate term to comprise both categories. Note that there is a structural difference between an antagonistic salt and a charged hydrotrope, although both types of electrolytes can have a salting-in behavior: a charged hydrotrope consists of one amphiphilic and one very hydrophilic ion, whereas an antagonistic salt consists of one hydrophobic and one hydrophilic ion.

Let us consider co-solubilizers in some more details: when they are mixed with water, various structures may appear, but not necessarily. In the simplest case, nothing significant occurs and the solution contains

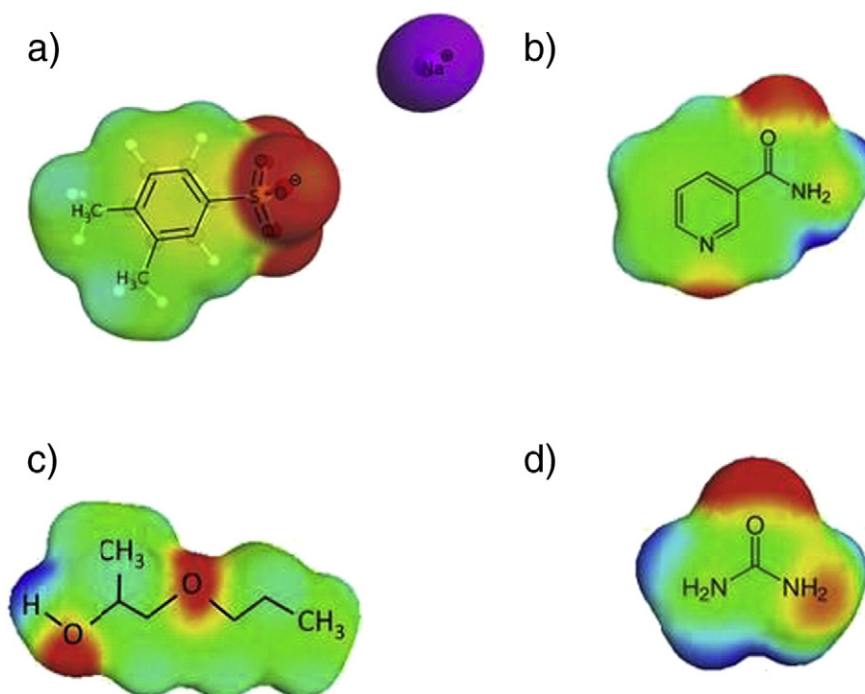


Fig. 1. Some examples of molecules that are commonly considered as hydrotropes. (a) Sodium xylenesulfonate (SXS), (b) nicotinamide, (c) propylene glycol *n*-propyl ether (PnP), (d) urea.

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